Study of electron scattering by CO_2 at the static-exchange level

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(Received 26 May 1981)

We present results for the scattering of low-energy electrons by CO_2 at the static-exchange level. The collision equations were solved by the iterative Schwinger method. All necessary partial-wave expansions have been carried out to high order so as to assure convergence of the scattering solutions. Of special interest are our calculated position and width for the $^2\Pi_u$ resonance of 5.39 and 0.64 eV, respectively, which differ significantly from previously published results.

I. INTRODUCTION

Collisions of low-energy electrons with CO_2 molecules are of significant experimental and theoretical interest. Morrison *et al.*[1] have studied the scattering of electrons by CO_2 in the energy range $0.07-10.0$ eV. In these studies, exchange and polarization effects in the scattering potential were approximated by a local energy-dependent potential and a semiempirical polarization potential, respectively. The coupled radial equations resulting from the partial-wave expansions of the wave function of the scattered electron and the potential were numerically integrated. Dill *et al.*[2] have used the continuum multiple-scattering model to study the scattering of electrons by CO_2. The emphasis of these studies was the role of shape resonance in the enhancement of vibrational excitation at intermediate energies in electron-molecule scattering. Among several approximations for the scattering potential the continuum multiple-scattering model also uses a local exchange approximation. Onda and Truhlar[3] have also reported differential and integral cross sections for electron-CO_2 elastic scattering at 20 eV. These studies used a semiempirical scattering potential.

In this paper we present the results of studies of the scattering of low-energy electrons by CO_2 in the static-exchange approximation. These studies were done with the iterative Schwinger variational method which we have recently developed for studying electron-molecule and electron-molecular ion collisions. Although these studies neglect the effects of polarization, we believe that it is important to determine the converged scattering solutions for the e^--CO_2 system at the static-exchange level. These static-exchange results are not only useful in several applications, such as in the calculation of vibrational excitation cross sections at energies where polarization effects are not dominant, and of electronic excitation cross sections, but they are also needed in order to realistically assess approximate schemes such as the local exchange approximation. It has also been shown that the static-exchange approximation with an appropriately distorted charge density derived from the negative-ion wave function can provide resonance vibrational excitation cross sections.[4,5]

In Sec. II we give a very brief outline of the method used in these studies. In Sec. III we present the $^2\Sigma_g$, $^2\Sigma_u$, $^2\Pi_u$, and $^2\Pi_g$ eigenphases at incident momenta of 0.1, 0.3, 0.5, 0.7, 0.8573, and 1.0. All the required matrix elements were evaluated with the use of single-center partial-wave expansions. In these studies of e-CO_2 scattering with its highly anisotropic interaction we have carried out the single-center expansions to high l values to assure that our results are converged. The eigenphase sums for the resonant $^2\Pi_u$ channel are of particular importance in this regard. The parameters for this $^2\Pi_u$ resonance extracted from our eigenphase sums are 0.64 eV for the width and 5.39 eV for the position. We also compare our calculated cross sections with measured elastic scattering cross sections.

II. THEORY

In these studies we use the iterative Schwinger variational method to solve the collision equations for the e-CO_2 system. Briefly, the iterative Schwinger variational method[6] is a method to solve the partial-wave Lippmann-Schwinger equation,

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$$\psi_{klm}^{(+)}=\phi_{klm}+G^{(+)}(E)U\psi_{klm}^{(+)} , \tag{1}$$

where ϕ_{klm} is a component of the incident plane wave, $G^{(+)}$ the Green's function with outgoing wave boundary conditions, and $U=2V$ with V the effective interaction between the target and the scattered electron. The partial-wave component of the total scattering wave function is defined by

$$\psi_{\vec{k}}^{(+)}=\left[\frac{2}{\pi}\right]^{1/2}\sum_{lm} i^l\psi_{klm}^{(+)}(\vec{r})Y_{lm}^*(\Omega_{\hat{k}}) . \tag{2}$$

The Schwinger variational expression for the partial-wave elastic T-matrix elements can be written as[7]

$$\tilde{T}_{ll'm}=\frac{\langle\phi_{klm}\mid U\mid\tilde{\psi}_{klm}^{(+)}\rangle\langle\tilde{\psi}_{klm}^{(-)}\mid U\mid\phi_{kl'm}\rangle}{\langle\tilde{\psi}_{klm}^{(-)}\mid U-UG^{(+)}U\mid\tilde{\psi}_{kl'm}^{(+)}\rangle} , \tag{3}$$

where $\tilde{\psi}_{klm}$ is a trial scattering function and we have assumed the molecule to be linear. Expansion of the trial scattering function in basis functions and variation of the linear expansion coefficients give the stationary result

$$T_{ll'm}^{S_0}=\sum_{\alpha_i,\alpha_j}^{N}\langle\phi_{klm}\mid U\mid\alpha_i\rangle \times[(D^{(+)})^{-1}]_{ij}\langle\alpha_j\mid U\mid\phi_{kl'm}\rangle , \tag{4}$$

where α's are the expansion functions and

$$D_{ij}^{(+)}=\langle\alpha_i\mid U-UG^{(+)}U\mid\alpha_j\rangle . \tag{5}$$

As is well known, the T matrix of Eq. (4) is equivalent to solving the Lippmann-Schwinger equation, Eq. (1), with a separable potential of the form

$$U^S(\vec{r},\vec{r}')=\sum_{\alpha_i,\alpha_j}\langle\vec{r}\mid U\mid\alpha_i\rangle(U^{-1})_{ij}\langle\alpha_j\mid U\mid\vec{r}'\rangle , \tag{6}$$

where the matrix of $(U^{-1})_{ij}$ is the inverse of the potential matrix U_{ij}. The corresponding approximate scattering solution of Eq. (1) is then

$$\psi_{klm}^{S_0}(\vec{r})=\phi_{klm}(\vec{r})+\sum_{\alpha_i,\alpha_j}\langle\vec{r}\mid G^{(+)}U\mid\alpha_i\rangle \times(D^{-1})_{ij}\langle\alpha_j\mid U\mid\phi_{klm}\rangle . \tag{7}$$

At this point we have obtained an approximate noniterative solution to the scattering equations. We have developed a method to iteratively improve the scattering function in Eq. (7).[6] As noted by Ernst *et al*,[8] if the expansion set used in Eqs. (6) and (7) contained the exact solution, then the solution given back by Eq. (7) would again be the exact solution. Then our iterative method proceeds by augmenting the expansion set used in Eq. (6) by including the approximate solutions $\psi_{klm}^{S_0}(\vec{r})$. Equation (7) will then yield a new and probably improved solution, $\psi_{klm}^{S_1}$, to Eq. (1). The next iteration proceeds in a similar fashion by replacing the solutions $\psi_{klm}^{S_0}$ in the expansion sets by those of the first iteration, $\psi_{klm}^{S_1}$. This new expansion set then yields a new set of approximate solutions $\psi_{klm}^{S_2}$. This procedure can be continued until convergence. Various criteria can be developed to establish when the exact solutions to the scattering equations have been obtained.[6]

III. RESULTS AND DISCUSSION

We have applied the Schwinger variational method in its iterative form to study the scattering of low-energy electrons by CO_2. For the scattering potential we use the static-exchange approximation which was obtained from an SCF (self-consistent-field) calculation in a $[3s\,2p\,1d]$ contracted Cartesian Gaussian basis.[9] The SCF energy for CO_2 in the basis is $-187.674\,286$ a.u. and the quadrupole moment is -4.013 a.u. for a C—O bond distance of 2.1944 a.u.

We have carried out calculations for the $^2\Sigma_g$, $^2\Sigma_u$, $^2\Pi_u$, and $^2\Pi_g$ eigenphases. The expansion functions used to construct the separable approximation to the scattering potential, Eq. (6), in the initial step of the iterative procedure are spherical Gaussian functions defined by

$$\phi_{lm}^{\alpha}(\vec{r})=N_{lm}^{\alpha}\mid\vec{r}-\vec{A}\mid^l e^{-\alpha\mid\vec{r}-\vec{A}\mid^2}Y_{lm}(\Omega_{\vec{r}-\vec{A}}) . \tag{8}$$

The spherical Gaussians, as defined in Eq. (8), can be expanded onto a different center by taking linear combinations of expansions of the appropriate Cartesian Gaussian functions.[10] However, for spherical Gaussian functions with larger values of l, the required expressions can be more easily obtained by noting that a spherical Guassian is the product of a simple s-type Gaussian function and a solution to Laplace's equation, both of which have

simple expressions for their expansion about another center.[10,11] The basis sets for the different symmetries are given in Table I. The total number of basis functions for the $^2\Sigma_g$, $^2\Sigma_u$, $^2\Pi_u$, and $^2\Pi_g$ symmetries are 30, 24, 19, and 19, respectively. All matrix elements were evaluated with the use of single-center expansions and Simpson's rule quadrature for the radial integrals. The grid for the quadrature contained 1000 points and extended out to 80 a_0. In the static potential partial waves through $l=59$ were retained while in the expansion of the occupied orbitals in the exchange kernel we used enough partial waves so that each orbital was normalized to better than 0.99. For the $1\sigma_g$, $2\sigma_g$, $3\sigma_g$, and $4\sigma_g$ orbitals this required l values up to 38, 10, 24, and 16, respectively, and l values up to 39, 23, 15, 15, and 16 for the $1\sigma_u$, $2\sigma_u$, $3\sigma_u$, $1\pi_u$, and $1\pi_g$ orbitals, respectively, in the exchange kernel. In the expansion of $1/r_{12}$ we retained partial waves up to $l=108$ in the direct potential and up to 40 in the exchange potential. The maximum partial retained in the expansion of all other functions in the calculation, e.g., in $\tilde{\psi}$, $V\tilde{\psi}$, and $GV\tilde{\psi}$, was $l=59$.

In Tables II–V we show the eigenphases and eigenphase sums at $k=0.1$, 0.3, 0.5, 0.7, 0.8573, and 1.0 for the $^2\Sigma_g$, $^2\Sigma_u$, $^2\Pi_u$, and $^2\Pi_g$ channels. These eigenphases were obtained from the second iteration of our iterative procedure and are quite well converged. We have chosen to show these results in tabular form since in this form they will be more useful for comparison with results of other approaches to the solution of the scattering equations or with the results of model calculations. To our knowledge the only other published eigenphases for e-CO_2 scattering in this energy range are those of the multiple-scattering model by Dill *et al.*[2] We do not compare the present static-exchange eigenphase sums with their results in any detail since their actual numerical values are not given.[2] However, several qualitative features of our results agree with theirs. For example, the increase in our σ_g eigenphase sum at around $k=1.0$ clearly also locates a high-energy shape resonance in this channel. The eigenphases of Table II show that the resonance contains a strong mixture of s, d, and g waves. The resonant behavior in the $^2\Pi_u$ eigenphase sum is due to the well-known shape res-

TABLE I. Basis sets used in the initial step of the iterative procedure.[a]

$^2\Sigma_g$ symmetry					$^2\Sigma_u$ symmetry				
Number of functions[b]	Center	l	m	Range of exponent	Number of functions	Center	l	m	Range of exponent
6	O	0	0	8.0–0.25	6	O	0	0	8.0–0.25
4	O	1	0	2.0–0.25	4	O	1	0	2.0–0.25
3	O	2	0	1.0–0.25	1	O	2	0	0.5
2	O	3	0	1.0–0.5	5	C	1	0	8.0–0.5
1	O	4	0	0.5	4	C	3	0	2,0–0.25
6	C	0	0	8.0–0.25	3	C	5	0	2.0–0.5
4	C	2	0	2.0–0.25	1	C	7	0	1.0
3	C	4	0	2.0–0.5					
1	C	6	0	1.0					
$^2\Pi_u$ symmetry					$^2\Pi_g$ symmetry				
5	O	1	1	4.0–0.25	5	O	1	1	4.0–0.25
4	O	2	1	2.0–0.25	4	O	2	1	2.0–0.25
5	C	1	1	4.0–0.25	5	C	2	1	4.0–0.25
4	C	3	1	2.0–0.25	4	C	4	1	2.0–0.25
1	C	5	1	0.5	1	C	6	1	0.5

[a]See Equation (8).

[b]Total number of basis functions on a given center with the same value of l and m. The exponents of the basis functions form a geometric series with a ratio of 2.0.

TABLE II. $^2\Sigma_g$ eigenphases and eigenphase sums for e-CO_2 collisions.

k[a]	δ_{sum}[b]	l_{max}[c]	δ_0[d]	δ_2	δ_4	δ_6	δ_8	δ_{10}
0.1	−0.15	10	−0.14	−0.01				
0.3	−0.47	24	−0.40	−0.04	−0.01	−0.01		
0.5	−0.76	38	−0.60	−0.10	−0.03	−0.01	−0.01	
0.7	−1.08	52	−0.71	−0.29	−0.03	−0.02	−0.01	−0.01
0.8573	−1.18	58	−0.46	−0.67	0.02	−0.03	−0.01	−0.01
1.0[e]	−0.88	58	−0.29	−0.82	−0.31	−0.03	−0.01	−0.01

[a]Incident momentum in a.u.
[b]Eigenphase sum.
[c]Dimensionality of the partial-wave K matrix used.
[d] δ_l is the eigenphase whose principal partial-wave component is l.
[e] Convergence not complete. This eigenphase sum could be in error by ± 0.01 radians.

onance in the e-CO_2 system. A simple fit of the eigenphase sums to a Breit-Wigner form including a background term gives a resonance position of 5.39 eV and a width of 0.62 eV. Experimentally[12] this shape resonance occurs at around 3.8 eV. This difference of about 1.6 eV between the position of this resonance in the static-exchange model and its actual location is obviously due to polarization effects. A difference of this magnitude is quite consistent with the results of similar studies of shape resonances in the e-N_2 and e-CO systems.[12,14] The multiple-scattering model predicts a resonance position of 3.4 eV in this $^2\Pi_u$ channel.

In Fig. 1 we compare our calculated total elastic scattering cross sections with those calculated with a local model exchange potential by Morrison *et al.*[1] A comparison of these cross sections show that with this local exchange approximation the $^2\Pi_u$ shape resonance comes out at about 8 eV which is about 3-eV higher than our calculated position of 5.39 eV. A semiempirical polarization potential with a single adjustable parameter was then added to this local exchange potential so as to move this shape resonance down to its experimental location of 3.8 eV. The present results, in which the $^2\Pi_u$ resonance is seen to be at around 5.4 eV at the static-exchange level, show that polarization effects have been overestimated in the semiempirical potential as used by Morrison *et al.*[1] Figure 1 shows that the magnitude and shape of the total elastic cross section obtained with the local exchange approximation[1] are quite different from the present calculated static-exchange values. To obtain the total elastic cross sections shown in Fig. 1 we added first-Born estimates for the $^2\Delta_g$ and $^2\Delta_u$ symmetries to the actual static-exchange contributions for the $^2\Sigma_g$, $^2\Sigma_u$, $^2\Pi_u$, and $^2\Pi_g$ channels. For comparison we also show in Fig. 1 measured values of the total elastic cross sections.[15,16]

In Fig. 2 we show the elastic differential cross sections for the scattering of 10-eV electrons by CO_2. These static-exchange cross sections agree well with the recent measured values of Register *et al.*[16]

TABLE III. $^2\Sigma_u$ eigenphases and eigenphase sums for e-CO_2 collisions.[a]

k	δ_{sum}	l_{max}	δ_1	δ_3	δ_5	δ_7	δ_9	δ_{11}
0.1	−0.088	9	−0.078	−0.009				
0.3	−0.35	23	−0.30	−0.03	−0.01			
0.5	−0.71	39	−0.63	−0.04	−0.02	−0.01		
0.7	−1.08	53	−0.99	−0.04	−0.02	−0.01	−0.01	
0.8573	−1.34	59	−1.25	−0.04	−0.02	−0.01	−0.01	
1.0	−1.55	59	−1.45	−0.02	−0.03	−0.02	−0.01	−0.01

[a]See footnotes for Table II.

TABLE IV. $^2\Pi_u$ eigenphases and eigenphase sums for e-CO_2 collisions.[a]

k	δ_{sum}	l_{max}	δ_1	δ_3	δ_5	δ_7	δ_9	δ_{11}
0.1	0.027	9	0.037	−0.009	−0.002	0.001		
0.3	−0.036	23	0.020	−0.034	−0.011	−0.005	−0.003	−0.002
0.5	−0.20	39	−0.18	0.03	−0.02	−0.01	−0.01	
0.5745	−0.13	45	−0.25	0.18	−0.02	−0.01	−0.01	
0.6083	0.24	47	−0.28	0.58	−0.02	−0.01	−0.01	
0.6403	1.59	49	−0.31	1.96	−0.02	−0.01	−0.01	
0.6708	2.12	51	−0.33	2.50	−0.02	−0.01	−0.01	
0.7	2.22	53	−0.053	2.82	−0.02	−0.01	−0.01	
0.8573	2.12	59	−0.62	2.82	−0.03	−0.01	−0.01	−0.01
1.0	1.92	59	−0.77	2.77	−0.03	−0.02	−0.01	−0.01

[a]See footnotes for Table II.

Recently, Schneider and Collins[17] reported some results from their preliminary static-exchange calculations for electron scattering by CO_2. Sepcifically, they report the $^2\Pi_u$ resonance at 8.2 eV with a width of 2 eV. They[17] also indicate that these results are converged to about 15%. These results differ significantly from our calculated position of 5.39 eV and a width of 0.64 eV. To try to understand these calculated positions and widths for this resonance we have repeated our calculation with a reduced number of partial waves in the various expansions in the evaluation of the matrix elements of Eq. (4). Specifically, the maximum partial wave retained in the expansion of any function in Eq. (4) was reduced from 59 to 27 while only partial waves up to 54 were retained in the expansion of $1/r_{12}$ in the direct potential. In the expansion of the occupied orbitals in the exchange potential we retained partial waves up to 4, 5, 5, and 6 for the σ_g, σ_u, π_u, and π_g orbitals, respectively. In the expansion of the continuum orbital in the exchange potential we retained partial waves up to $l=5$. With these reduced partial-wave expansions we obtained eigenphase sums which give a resonance position of 7.33 eV and a width of 1.47 eV. This change of about 2 eV and 0.83 eV in the position and width of the resonance, respectively, due to the reduction in the partial-wave expansions suggest that the results of Schneider and Collins[17] may not be adequately converged. We also note that Čadež *et al.*[18] found that with a value of 0.31 eV for the width of this resonance at the ground-state equilibrium geometry in the boomerang model[19] they could accurately describe the observed resonant vibrational excitation cross section at 4-eV impact. A static-exchange value of 0.64 eV for the width of the resonance seems quite consistent with their assumed value of 0.31 eV since one expects polarization effects to reduce the static-exchange width by about a factor of 2, e.g., in the e-N_2 system.[5] Cal-

TABLE V. $^2\Pi_g$ eigenphases and eigenphase sums for e-CO_2 collisions.[a]

k	δ_{sum}	l_{max}	δ_2	δ_4	δ_6	δ_8	δ_{10}	δ_{12}
0.1	−0.014	10	−0.012	−0.003	0.001			
0.3	−0.065	24	−0.040	−0.012	−0.006	−0.003	−0.002	−0.001
0.5	−0.16	38	−0.11	−0.02	−0.01	−0.01		
0.7	−0.32	52	−0.25	−0.03	−0.01	−0.01	−0.01	
0.8573	−0.47	58	−0.39	−0.03	−0.01	−0.01	−0.01	
1.0	−0.59	58	−0.53	0.02	−0.03	−0.01	−0.01	−0.01

[a]See footnotes for Table II.

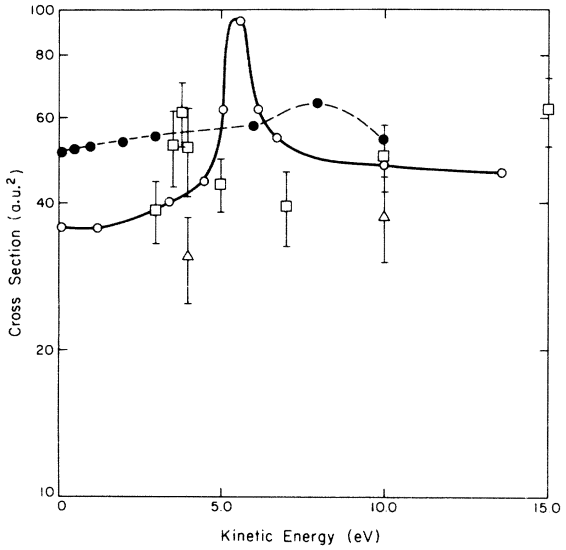

FIG. 1. Total elastic cross section for e-CO_2 scattering: ——○—— exact static-exchange results of present study; — — —●— — — static plus model exchange from Ref. 1; □ experimental data from Ref. 15; △ experimental data from Ref. 16.

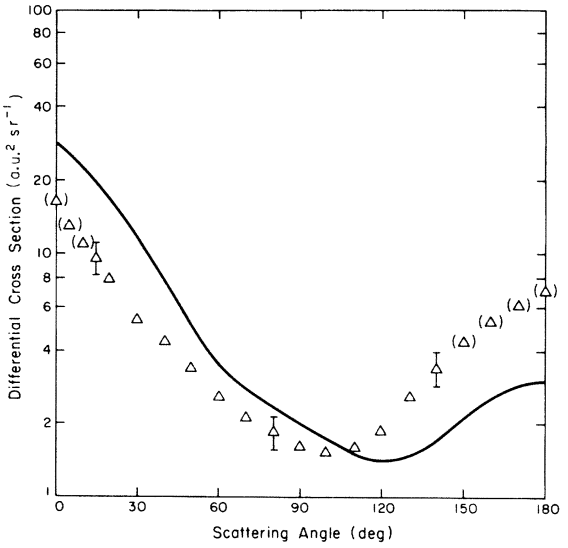

FIG. 2. Elastic differential cross section for scattering 10-eV electrons by CO_2: —— exact static-exchange results of present study; △ experimental data from Ref. 16, (△) indicates an extrapolated value.

culations which include such polarization effects in e-CO_2 collisions are under way.

ACKNOWLEDGMENTS

This research is based upon work supported by the National Science Foundation under Grant No. CHE79-15807. One of us (R. R. L) acknowledges support from Exxon Educational Foundation Fellowship. The research reported in this paper made use of the Dreyfus-NSF Theoretical Chemistry Computer which was funded through grants from the Camille and Henry Dreyfus Foundation, the National Science Foundation (Grant No. CHE78-20235), and the Sloan Fund of the California Institute of Technology. This research was also supported in part by an Institutional Grant from the United States Department of Energy, No. EY-76-G-03-1305.

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